

## Organochlorine Residues in Adipose Tissue of Chamois from the Catalan Pyrenees, Spain

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Organochlorine chemicals, including pesticides and industrial products, have been found to be present in aquatic (Martineau et al. 1987, Muir et al. 1988) and terrestrial (Brunn et al. 1985, Mason et al. 1986) mammal species. Although some of these animals are not edible or not specially important as a source of proteins for human or domestic animals, the detection of accumulated organochlorine compounds in their bodies is useful to control the grade of extension and to monitor the evolution of these xenobiotics in biosphere (Dowd et al. 1985, Somers et al. 1987). Data on this subject in south-west european non-migratory mammalian wildlife, is for the most part unknown.

The chamois or "izard" (Rupicapra rupicapra) is a typical inhabitant of many euroasiatic high mountains. They are consumers of alpine herbs, leaves of trees and bushes, and can be considered as intermediate animals in the food chain. Chamois are relatively sedentary; therefore their organochlorine residue profile may serve as an indicator for the level of contamination in their habitats, and can also be representative for the european non-carnivore mammalian wildlife.

There are two subspecies of chamois in Spain. The pyrenean chamois (R. rupicapra pyrenaica) is fortunately present in sufficient number in some zones of the Catalan Pyrenees, that its hunting for population control is allowed during a short period of the year. The Natural Park of Cadí-Moixeró is one of these zones: located in the north of Catalonia, near the frontier with France and Andorra, its extension is 413 km<sup>2</sup> and the height range from 900 to 2,647 m. Only an insignificant part of its soil is dedicated to

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agricultural uses, and no industries are found inside or near its domain.

The purpose of this work is to present organochlorine residue data for chamois collected in this zone.

## MATERIALS AND METHODS

Chamois were shot down in the Natural Park of Cadí-Moixeró by authorized hunters, under supervision of personnel of the Park. All the animals were hunted between September and December 1987. Samples of perirenal adipose tissue (10-30 g) were collected in situ and kept in hexane-cleaned glass vessels with teflon cap, and frozen as soon as possible. They were sent to our laboratory and stored at  $-18^{\circ}\text{C}$  until analyses. Nineteen samples were examined, corresponding to 16 males and 3 females, ranging 0.5-11 years ( $5.9 \pm 2.3$ , mean  $\pm$  S.D.).

Analyses were carried out following the method of cleanup with sulfuric acid of Veierov and Aharonson (1980). Although some organochlorine residues are lost with this method (Murphy 1972, Veierov and Aharonson 1980), the low concentrations found in adipose tissue of chamois recommend its use in order to avoid contamination from adsorbents and high volume of solvents needed for alternative cleanup methods.

All solvents were residue analysis grade or similar, and all glass vessels were washed with detergents and rinsed with distilled water, acetone and hexane before use. Anyway, blanks following the fully analytical steps were intercalated every 4-6 samples of adipose tissue in order to assess purity of the materials employed in the determinations.

Samples were analyzed on a Perkin-Elmer model 8500 gas chromatograph. A fused silica column (0.53 mm ID and 15 m long) coated with SPB-608 stationary phase (0.5  $\mu\text{m}$  film thickness) (Supelco, Bellefonte, PA), coupled to an electron capture detector (ECD), was used for analyses. Initial oven temperature was  $150^{\circ}\text{C}$ , maintained for 5 min, and programmed to  $280^{\circ}\text{C}$  at  $8^{\circ}\text{C}/\text{min}$ . Carrier and make-up gas (both  $\text{N}_2$ ) flows were 3 and 50 mL/min, respectively. Injector temperature was  $290^{\circ}\text{C}$  and ECD temperature was  $320^{\circ}\text{C}$ . Further confirmation of the identification of some of the peaks in the samples was made on another capillary column, coated with OV-73 stationary phase, in similar chromatographic conditions.

Fifteen pure pesticide standards, including insecticides and their metabolites, and hexachlorobenzene (HCB), were used in the analyses (Promochem, Wesel, FRG). We also examined the polychlorinated biphenyls (PCB) Aroclor<sup>®</sup> 1248 and 1254 (Alltech Ass., Deerfield, IL). All of them were used for recovery and calibration studies. Recoveries with fortified samples showed values that ranged from 80 to 114% ( $n = 5$ ) for all residues except endrin and dieldrin (0%), HCB (71%) and heptachlor-epoxide (75%); only for these two last residues corrections were introduced in quantifications. Calculations were made relative to an internal standard (op'DDE, previously showed non present in adipose tissue samples), added to the sample from the beginning. Variability, in terms of coefficient of variation of repeated analyses ( $n = 5$  to 15), was lower than 10% and considered satisfactory. The limit of detection was between 0.5 and 5 pg (latter value being for PCB) injected in the chromatographic system.

## RESULTS AND DISCUSSION

Levels of organochlorine chemicals in adipose tissue from chamois were very low, in the order of only a few parts per billion, as shown in Table 1. To our knowledge, there are no previous reports on organochlorine residue levels in chamois, but comparisons with other animal species can be made.

Only HCB, PCB and pp'DDE were found in the 100% of the samples, being the occurrence of all other residues lower than this value. The PCB profile was very close to that of the members of the Aroclor<sup>®</sup> 1254 family: the samples show 4 or 5 of the 5 major peaks of that standard.

With the exception of 1 sample, HCB was the main residue found in adipose tissue from chamois. This finding agree with previous reports on several domestic species and also with human beings from the northeast of Spain (To-Figueras et al. 1986, Gómez-Catalán et al. 1987), where HCB represents the major or one of the major residues, and confirms the preoccupant wide distribution of this chemical residue in Spain. The concentration range of 6.61-79.05 ppb is not, from an absolute point of view, high (Somers et al. 1987, Muir et al. 1988) nor near toxic levels for this compound in mammal species (Burton and Bennett 1987). However, taking into account the intermediate position of chamois in the food chain and their privileged wild habitat, the concentration found is probably higher than initially expected. Sources of environmental

**Table 1.** Organochlorine residue levels determined in adipose tissue of chamois (n = 19, ng/g wet weight).

		POSITIVE MEAN %	S.D.	S.E.M.	RANGE (min-max)
HCB	100	31.03	22.39	5.28	6.61-79.05
PCB	100	12.32	8.93	2.10	2.87-30.36
pp'DDE	100	2.06	1.28	0.30	0.79- 6.42
$\alpha$ -HCH	95	1.07	0.72	0.18	N.D.- 2.49
$\tau$ -HCH	95	0.99	0.76	0.18	N.D.- 3.37
Heptachlor-epox.	89	0.39	0.30	0.07	N.D.- 1.23
Heptachlor	68	0.44	0.22	0.06	N.D.- 0.73
$\beta$ -HCH	47	0.78	0.55	0.19	N.D.- 1.96
pp'DDT	37	1.07	0.47	0.19	N.D.- 1.81
Aldrin	26	0.11	0.02	0.01	N.D.- 0.14
op'DDD	21	0.50	0.37	0.21	N.D.- 1.02
pp'DDD+op'DDT	5	0.45	----	----	N.D.- 0.45

Mean = Arithmetic mean; S.D. = Standard deviation; S.E.M. = Standard error of the mean; N.D. = Not detected (below limit of detection). Note: mean, S.D. and S.E.M. have been calculated without inclusion of levels below limit of detection.

pollution for HCB seem to be diverse (Burton and Bennett 1987) and require further investigation, because of the potential carcinogenic effect of this compound (Cabral et al. 1977).

No significative correlations were found between HCB, PCB or pp'DDE levels and age ( $r < 0.5$  and  $p > 0.05$ ). However, a positive correlation, not due to experimental error, was found between levels of these three main residues:  $r = 0.83$  between HCB and PCB,  $r = 0.65$  between HCB and pp'DDE, and  $r = 0.46$  between PCB and pp'DDE, all of them with a  $p < 0.05$ . Similar correlations were obtained by McEwen et al (1984) in birds from the USA. Being the origin of this three residues very diverse (pesticide and/or industrial), this finding strongly suggests the non-existence of a punctual source of contamination in the zone, and thus an atmospheric origin for those chemicals.

For each individual sample, the ratio of concentrations pp'DDE/pp'DDT, and to a lesser extent the ratio heptachlor epoxide/heptachlor, seems to demonstrate the ancient use of the parent pesticides, theoretically not in use in Spain since 1977. On the other hand, the relatively high levels of lindane ( $\tau$ -HCH) in comparison

with their  $\alpha$  and  $\beta$  isomers, probably reflect the still wide use of this insecticide. The prevalence of the  $\alpha$  over the  $\beta$  isomer of HCH has been previously reported in other wild mammals, as otters (Somers et al. 1987) and marine mammals (Muir et al. 1988). In fact, the general pattern and concentrations of organochlorine pesticides determined in adipose tissue of chamois agree with those determined in otters from Canada (Somers et al. 1987), in spite of their very different geographical situation and respective positions in the food chains.

In conclusion, the total concentration of organochlorine residues stored in adipose tissue of chamois (around 50 ppb) are lesser than those found in several terrestrial mammalian species (Brunn et al. 1985, Mason et al. 1986, Somers et al. 1987) of other zones of the world, thus indicating that the area covered by the Natural Park of the Cadí-Moixeró is, in general, well-preserved from contamination with organochlorine chemicals.

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